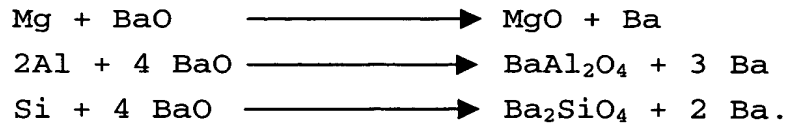## CATHODE-RAY TUBE CATHODE AND ALLOY THEREFOR

The invention relates to cathode-ray tube oxide cathodes, used as sources of electrons emitted by the thermionic effect, and more particularly to the

5   composition of the metal forming the basis of the cathode.

Background Of The Invention

A conventional oxide cathode consists of a layer of alkaline-earth oxides, such as a mixture of barium

10   oxide (BaO), strontium oxide (SrO) and calcium oxide (CaO) or a mixture of BaO and SrO, which is deposited on a basis metal made of nickel or a nickel alloy and comprising one or more reducing elements, such as mag- nesium (Mg), aluminium (Al), silicon (Si), chromium

15   (Cr), zirconium (Zr) or any other element capable of reducing oxides. The alkaline-earth oxide mixture may itself be doped with other oxides, such as, for example, Sc_2O_3 and Y_2O_3.

A conventional oxide cathode is constructed of a

20   tube made of a Ni alloy (generally Ni-Cr) to which a cap made in the basis metal is welded. Deposited on the basis metal is a layer made of a mixture of Ba and Sr carbonates or a mixture of Ba, Sr and Ca carbonates. These carbonates, which are stable in air, are

25   subsequently converted to oxides in the vacuum inside the cathode-ray tube. This oxide layer, heated to a cathode working temperature of approximately 800°C, becomes the electron-emitting layer when some of the BaO is converted to barium metal.

30   The formation of barium metal is maintained by the following mechanisms: the cathode, during operation, is heated to a temperature of approximately 800°C, causing the reducing elements to diffuse towards the interface between the nickel and the alkaline-earth oxides. These

35   reducing elements, for example, Mg, Al and Si, constantly react with the barium oxide and reduce it, in order to form barium metal according to the reactions:

$$Mg + BaO \longrightarrow MgO + Ba$$
$$2Al + 4\ BaO \longrightarrow BaAl_2O_4 + 3\ Ba$$
$$Si + 4\ BaO \longrightarrow Ba_2SiO_4 + 2\ Ba.$$

The reducing elements added to the nickel are therefore consumed by the chemical oxidation-reduction

5 reactions with BaO. The lifetime of the cathode is directly connected with the consumption of these elements so that, for each of the addition reducing elements chosen, a minimum content is desirable in order to guarantee a minimum lifetime. Furthermore, it

10 is known that some of the compounds resulting from the Ba reduction reactions described above, such as Ba_2SiO_4 or $BaAl_2O_4$, are so highly stable that they can accumulate at the interface [A. Eisenstein, H. John et al., J. Appl. Phys., T.24, No. 5, p. 631, 1953] between

15 the nickel and the alkaline-earth oxides. These compounds, because of their high resistivity, increase the impedance of the interface, thereby reducing the current density of the cathode. In addition, they degrade the lifetime of the cathode because they

20 permanently accumulate at the interface during operation of the cathode. By accumulating, they limit the diffusion of the reducing elements and thus decrease the reactions between the latter and BaO, which in turn reduces the amount of Ba metal formed,

25 which is necessary for emission [E.S. Rittner, Philips Res. Rep., T.8, p. 184, 1953]. Another major drawback is that an excessively high accumulation of these compounds may degrade the adhesion of the alkaline-earth oxides to the nickel.

30 The invention aims to avoid these drawbacks by properly choosing a composition of the material forming the basis of the cathode, which material consists of a nickel alloy for which the content of reducing elements must be chosen within a defined weight concentration

35 range according to the elements in question. Each

reducing element is added to the nickel in a concentration range defined by a lower limit and an upper limit, which range guarantees a long lifetime as well as optimum emission performance and reliability.

5   To achieve this result, the metal alloy according to the invention, intended for the manufacture of cathodes for cathode-ray tubes, mainly comprises nickel, together with magnesium (Mg), the weight concentration C_{Mg} of which is between 0.01% and 0.1%. Advantageously,

10 it also includes aluminium, the weight concentration C_{Al} of which satisfies the relationship:

$$C_{Al} \leq 0.14 \times (0.1 - C_{Mg}),$$

15   where:

- C_{Mg} is the Mg concentration in the nickel expressed as a percentage by weight;

- C_{Al} is the Al concentration in the nickel expressed as a percentage by weight.

20   Brief Description Of The Drawings

The invention and its various advantages will be more clearly understood with the help of the description below and of the drawings in which:

- Figure 1 illustrates an electron gun for a

25 cathode-ray tube;

- Figure 2 is a longitudinal section through an oxide cathode according to the invention.

Detailed Description Of The Preferred Embodiments

A cathode-ray tube comprises at least one source

30 for creating an electron beam intended to scan the tube's screen in order to excite phosphors thereon, these being intended to create a visible image.

As shown in Figure 1, the tube's gun 1 therefore comprises at least one cathode 2 and a succession of

35 electrodes (3, 4, 5, 6, etc.) which are intended to form the electron beam or beams 7, 8, 9 and to focus it or them onto the screen of the tube.

As shown in Figure 2, the cathode 2 is generally
in the form of an approximately cylindrical hollow tube
10, made of nickel or nickel alloy, for example nickel-
chromium. The tube 10 is closed at one of its ends by a
5 cap 11 which may be either an attached metal piece or
an integral part of the tube, obtained by drawing. The
cap is made of a nickel alloy and serves as a support
for the emissive layer 12 of alkaline-earth oxides.
This layer 12, heated to high temperature by the
10 filament 13, becomes the source of the electron beam
intended to scan the surface of the tube's screen.

When the nickel of conventional oxide cathodes is
heated, compounds may form, not only as a result of the
reduction of the barium oxide BaO by reducing elements,
15 but also by direct reaction of the reducing elements,
with the residual oxygen present in the nickel or with
the oxygen present in the atmospheres to which the
nickel is exposed during the various steps in the
production of the cathodes. For example, the production
20 of cathodes usually includes a step of annealing the
basis metal in hydrogen at a temperature close to
1000°C. The water (H_2O) content of the hydrogen is
generally very low, so that the atmosphere is reducing
for nickel at the annealing temperature. On the other
25 hand, the H_2O content, even if it is reducing for
nickel, may be sufficient to oxidize the reducing
elements present in the nickel, such as Mg and Al.
Magnesia (MgO) and alumina (Al_2O_3) thus form on the
surface of the nickel during annealing. More complex
30 compounds resulting from the reaction of two reducing
elements with oxygen are also observed, for example,
$MgAl_2O_4$ or $BaAl_2O_4$, the latter being observed as a result
of the chemical reaction of the reducing elements with
the alkaline-earth oxides. The formation of these
35 compounds was studied together with their persistence
during the step of activating the cathode in the
cathode-ray tube. During this activation step, the
cathode is heated in the vacuum of the cathode-ray tube

(typically, $P < 10^{-6}$ torr) at a maximum temperature of between 900°C and 1100°C. The purpose of this operation is, on the one hand, to convert the carbonates to oxides and, on the other hand, to optimize the electron

5   emission of the cathode. For nickels of various Mg and Al compositions, the compound $MgAl_2O_4$ is formed during the hydrogen annealing step at the interface between the basis metal of the cap 11 and the coating of emissive oxides. This compound is a stable compound and

10   is in the form of small crystallites partially covering the nickel surface and having a tendency to accumulate at the interface during the life of the cathode.

Since this type of stable compound is deleterious, its presence at the interface must be limited as far as

15   possible so as to maintain good adhesion of the oxide layer to the basis metal.

The amount of crystallites was determined by image analysis on images of nickel surfaces taken in a scanning electron microscope (SEM). The percentage of

20   surface covered by the crystallites could be measured by image analysis since these crystallites appear white against a black nickel background. This percentage was measured after the activation step in the cathode-ray tube; that is to say, it represents the crystallites

25   which persist after activation and are present at the start of the cathode's life.

Statistical analysis of the experimental measure-ments of the amount of coverage by the crystallites present on the surface of the basis metal after the

30   activation carried out on several nickel castings has shown that it is relevant to link the amount of coverage by stable crystallites to the magnesium and aluminium concentrations of the basis metal.

Results from this analysis have led to the

35   equation which represents this percentage of surface coverage, and therefore the amount of surface crystal-lites, as a function of the aluminium content and the magnesium content in the alloy forming the basis metal:

$$C_s = [-2 + (50 \times C_{Mg}) + (350 \times C_{Al})]\% \qquad (1)$$

5

where:

 - C_s is the percentage of nickel surface covered by crystallites;

 - C_{Mg} is the Mg concentration in the nickel

10 expressed as a percentage by weight;

 - C_{Al} is the Al concentration in the nickel expressed as a percentage by weight.

 It is common practice to have a minimum magnesium

15 content in the nickel since magnesium is highly reducing and diffuses very rapidly. Consequently, magnesium ensures that the cathode is activated quickly during the activation process described above and ensures proper electron emission during the first few

20 hundred or so hours of the cathode's life. Since magnesium has this favorable behavior, it is preferable, in order to limit the amount of $MgAl_2O_4$ crystallites, to optimize the Al content rather than limit the magnesium content.

25 The magnesium content may advantageously be set to a value of between 0.01% and 0.1%. Knowing, from experience, that the maximum percentage of stable crystallites considered as acceptable, that is to say, giving good adhesion of the oxide layer to the basis

30 metal, is 3%, the maximum Al content of the nickel alloy according to the invention is calculated from the magnesium content, using the following equation derived from equation(1):

35     $C_{Al} \le 0.14 \times (0.1 - C_{Mg}). \qquad (2)$

 The following table shows the variations in the adhesion of the oxide layer according to the various

magnesium and aluminium contents in the basis metal. Good adhesion is therefore well guaranteed when the inequality (2) is satisfied.

Mg (wt%)	Al (wt%)	0.14 [0.1-C_{Mg}] (wt%)	Measured crystallites (% of surface)	Calculated crystallites (% of surface)	Oxide layer / basis metal adhesion
0.0085	0.006	0.01281	0.05	0.525	Good
0.014	0.003	0.01204	0.025	-0.25	Good
0.02	0.006	0.0112	0.5	1.1	Good
0.025	0.003	0.0105	0.35	0.3	Good
0.028	0.006	0.01008	0.45	1.5	Good
0.03	0.013	0.0098	4.9	4.05	Occasional faults
0.031	0.004	0.00966	1.3	0.95	Good
0.032	0.008	0.00952	3.2	2.4	Good
0.032	0.011	0.00952	5.5	3.45	Occasional faults
0.04	0.02	0.0084	6	7	Occasional faults
0.056	0.003	0.00616	1.4	1.85	Good

Table: percentage of nickel surface covered by crystallites for various magnesium and aluminium contents in the nickel (measured values and values calculated from equation (1)).